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A Simple Preparation and Catalytic Properties of Colloidal Nickel for Selective Hydrogenation[1)]

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Colloidal nickel was easily prepared by reaction of nickel bromide with zinc powder under a nitrogen atmosphere. *N,N*-Dimethylformamide was a favorable solvent for the reaction. A simple and convenient method for selective hydrogenation using the colloidal nickel has been investigated. Phenylacetylene was successively hydrogenated to give ethylbenzene *via* styrene under an atmospheric pressure of hydrogen. Diphenylacetylene was similarly reduced to afford dibenzyl *via* (*Z*)-stilbene. *p*-Bromonitrobenzene was successively hydrogenated to give aniline *via* *p*-bromoaniline in the presence of the catalyst.

KEY WORDS: Successive hydrogenation/ Metallic nickel/ Phenylacetylene/

INTRODUCTION

Recently, selective hydrogenations have been studied on the hydrogenation of alkynes catalyzed by metal catalysts, such as Ca,[2)] Fe,[3)] Ni,[4-6)] Ru,[7)] Pd,[8-11)] and Pt[9,10)] catalysts. In the previous papers we have found that metallic nickel (colloidal state) generated from nickel halides and zinc powder was active for the hydrogen transfer reaction of cyclohexadienes[12)] and for the hydrogenation of aromatic nitro compounds.[1)] In this paper we wish to report successive hydrogenation of phenylacetylenes and *p*-bromonitrobenzene using the colloidal nickel. The advantages of this procedure are the easy and economical access to the reagents and no need of pressure apparatus.

EXPERIMENTAL

Materials. Anhydrous nickel bromide, zinc powder, phenylacetylenes, and nitrobenzenes were commercially available. *N,N*-Dimethylformamide (DMF) was distilled over calcium hydride under nitrogen before use. Other solvents were purified by ordinary methods.

General Procedure. To a 50 cm^3 flask fitted with a septum inlet and a magnetic stirbar were added anhydrous nickel bromide (0.2 mmol), zinc powder (1 mmol), and DMF (15 cm^3). After the atmosphere was replaced with nitrogen the catalyst mixture was allowed to stand overnight at room temperature. The mixture became a black solution containing fine metallic nickel. A hydrogen buret was connected to the flask and the atmosphere was replaced with hydrogen. To the mixture phenylacetylene (6 mmol) in DMF (5 cm^3) was added. The mixture

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was stirred with a magnetic stirrer at 800 revolutions per minute and kept in a thermostated bath. The reaction was stopped by shaking in the air. After centrifuging, the supernatant was subjected to GLC analysis.

Analysis. The gas chromatographic analyses were performed on a Shimadzu GC-8A instrument with a TC detecter and helium carrier gas using a 3 m column of polyethylene glycol 20M or ethylene glycol succinate by the internal standard methods.

RESULTS AND DISCUSSION

Preparation of Colloidal Nickel and Its Catalytic Activities. Under a nitrogen atmosphere colloidal nickel was prepared by treating a suspension of anhydrous nickel bromide in DMF with zinc powder. When the mixture was allowed to stand overnight at room temperature, nickel (II) was reduced to metallic nickel. The mixture became a black solution containing fine metallic nickel (colloidal nickel). The effect of the ratio of Zn/Ni (II) on the hydrogenation of phenylacetylene is shown in Fig. 1. No catalytic activities for hydrogenation was found in the absence of nickel bromide or zinc powder. Therefore, the catalytic species was colloidal nickel prepared by adding excess zinc powder to nickel (II). A high catalytic activity was obtained by reducing nickel (II) with three to five equivalents of zinc powder.

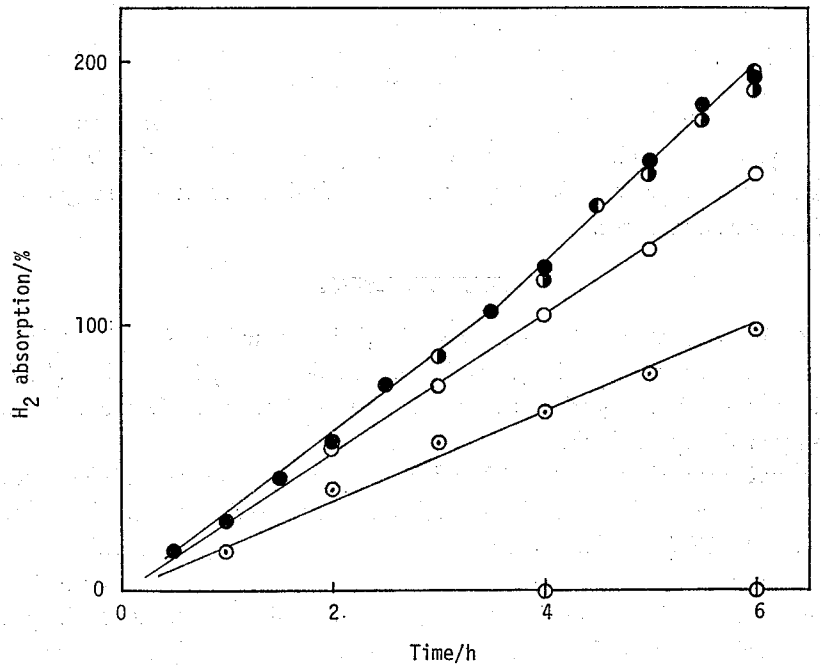

Fig. 1. Effect of the amount of Zn added to Ni(II) on the hydrogenation of phenylacetylene.
Phenylacetylene 6 mmol, $NiBr_2$ 0.2 mmol, DMF 20 cm^3, temp 50°C, under an atmospheric perssure of H_2.
Zn (mmol)——◑: 2, ●: 1, ◑: 0.6, ○: 0.22, ⊙: 0.1, ⊕: 0 or 1 (Zn alone).

Table 1. Effect of Solvent on the Hydrogenation of Phenylacetylene Catalyzed by Colloidal Nickel[a)]

Solvent	Time	Conv	Yield/%[e)]	
	h	%	Styrene	Ethylbenzene
DMF	3.5	100	91	5
DMF	6	100	0	98
EtOH	3.5	94	77	8
EtOH	6	100	0	95
HMPA[b)]	5	90	80	5
MeOH	6	25	23	0
DMSO[c)]	5	18	18	0
THF[d)]	6	15	11	4

a) Reaction conditions; phenylacetylene 6 mmol, $NiBr_2$ 0.2 mmol, Zn 1 mmol, solvent 20 cm^3, temp 50°C, under an atmospheric pressure of H_2.
b) Hexamethylphosphoric triamide.
c) Dimethyl sulfoxide.
d) Tetrahydrofuran.
e) The yields were determined by GLC analysis.

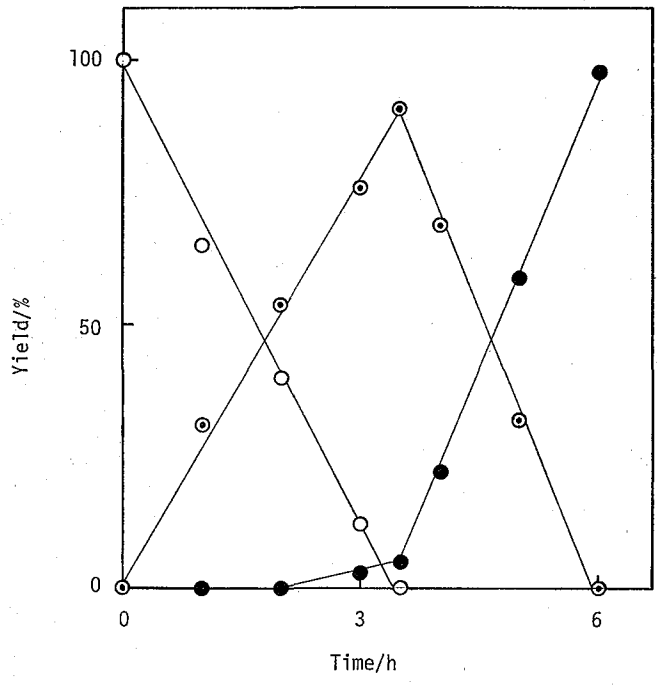

Fig. 2. Hydrogenation of phenylacetylene catalyzed by colloidal nickel. Phenylacetylene 6 mmol, $NiBr_2$ 0.2 mmol, Zn 1 mmol, DMF 20 cm^3, temp 50°C, under an atmospheric pressure of H_2.
○: Phenylacetylene, ⊙: styrene, ●: ethylbenzene.

The effect of solvent on the hydrogenation of phenylacetylene is shown in Table 1. The most favorable solvent for the reaction was DMF. In DMF phenylacetylene was successively hydrogenated to give ethylbenzene *via* styrene. Ethanol and hexamethylphosphoric triamide (HMPA) were good solvents for the hydrogenation. However, in alcohols colloidal nickel precipitated gradually from the reaction mixture with the elapse of time. A little hydrogenation occurred in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO).

Successive Hydrogenation. Under an atmospheric pressure of hydrogen phenylacetylene was successively hydrogenated to give ethylbenzene *via* styrene in the presence of colloidal nickel, as shown in Fig. 2. In the first stage of hydrogenation phenylacetylene was selectively hydrogenated to give styrene and secondly styrene formed was hydrogenated to afford ethylbenzene: Styrene was obtained in a 91% yield at 3.5 h and ethylbenzene was done in a 98% yield at 6 h. The hydrogenation rate of styrene was comparable to that of phenylacetylene.

$$RC\equiv CR' \xrightarrow[\text{under } H_2 \text{ atmosphere}]{NiBr_2\text{-Zn in DMF}} \underset{((Z)\text{-form})}{RCH=CHR'} \longrightarrow RCH_2CH_2R'$$

$$XC_6H_4NO_2 \xrightarrow[\text{under } H_2 \text{ atmosphere}]{NiBr_2\text{-Zn in DMF}} XC_6H_4NH_2 \longrightarrow C_6H_5NH_2\cdot HX$$

Table 2. Successive Hydrogenation Catalyzed by Colloidal Nickel

Substrate	Temp / °C	Time / h	Product (yield/%)[c]
Phenylacetylene[a]	50	3.5	Styrene (91) Ethylbenzene (5) Phenylacetylene (0)
Phenylacetylene[a]	50	6	Styrene (0) Ethylbenzene (98) Phenylacetylene (0)
Diphenylacetylene[a]	50	3.5	(*Z*)-Stilbene (80) (*E*)-Stilbene (0) Dibenzyl (8) Diphenylacetylene (9)
Diphenylacetylene[a]	50	10	(*Z*)-Stilbene (0) (*E*)-Stilbene (3) Dibenzyl (96) Diphenylacetylene (0)
Nitrobenzene[b]	130	8	Aniline (97) Nitrobenzene (0)
p-Bromonitrobenzene[b]	130	10	*p*-Bromoaniline (94) Aniline hydrobromide (0) Nitrobenzene (0) *p*-Bromonitrobenzene (0)
p-Bromonitrobenzene[b]	130	45	*p*-Bromoaniline (4) Aniline hydrobromide (92) Nitrobenzene (0) *p*-Bromonitrobenzene (0)

a) Reaction conditions; substrate 6 mmol, $NiBr_2$ 0.2 mmol, Zn 1 mmol, DMF 20 cm^3, under an atmospheric pressure of H_2.
b) Ref. 1. Reaction conditions; substrate 10 mmol, $NiBr_2$ 1 mmol, Zn 5 mmol, DMF 50 cm^3, under an atmospheric pressure of H_2.
c) The values in parenthesis are yields determined by GLC analysis.

Successive hydrogenations catalyzed by colloidal nickel are listed in Table 2. The catalyst has a high activity for successive hydrogenation. In the first stage of hydrogenation diphenylacetylene was exclusively hydrogenated to give (*Z*)-stilbene in a 80% yield at 3.5 h. Then, it was reduced to provide dibenzyl in a 96% yield at 10 h with a slight (*Z*)-(*E*) isomerization. In the case of aromatic nitro compounds nitrobenzene was hydrogenated to give aniline in a high yield (97%) and *p*-bromonitrobenzene was successively reduced to afford aniline *via* *p*-bromoaniline.

In conclusion, colloidal nickel simply prepared by reaction of nickel bromide with zinc powder has a high activity for successive hydrogenation.

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